FEASIBILITY STUDY OF MTBE PHYSICAL ADSORPTION FROM POLLUTED WATER ON GAC, PAC AND HUSK RICE CARBON IN BATCH PROCESS

Omid Mowla[1], Ayoub Karimi Jashni[2]

[1]*Department of Civil Engineering, Science and Research Branch, Islamic Azad University, Fars, Iran*
[2]*Civil and Environmental Engineering Department, Shiraz University, Shiraz, Iran,*

Abstract

MTBE or Methyl Tertiary Butyl Ether is an organic compound, which is used to increase the gasoline Octane Number. At the beginning of 80's, by discovering the undesirable effects of tetra ethyl lead usage in fuel, MTBE started to be used worldwide. But gradually the undesirable effects of MTBE on environment had been revealed.

There are many technologies for MTBE removal from polluted water. Adsorption is the most conventional and economical technology. In this research, some experiments have been done for studying the adsorption of MTBE on different solid adsorbent in batch process. In these experiments a fixed amount of adsorbents including Granular Activated Carbon (GAC), Powdered Activated Carbon (PAC) and the Husk Rice Carbon (HRC) have been put in different one litter covered vessels containing water polluted with known initial MTBE concentration and stirring them. By measuring MTBE concentration in the vessel at different times the effect of different operating parameters such as temperature and pH have been studied on adsorption and optimum condition have been determined. The batch experimental results have been used to calculate the constant parameters of Freundlich and Langmuir adsorption isotherm equations for these systems.

***Keywords:** MTBE, Adsorption, Activated Carbon, Husk Rice Carbon*

--***--

1. INTRODUCTION

MTBE or Methyl Tertiary Butyl Ether (C5H12O) is an organic compound with oxygen in its chemical structure which is colorless, flammable and combustible in normal pressure and temperature. With molar mass of 88.15 gr/mol its melting point is -9 C° and boiling point is 55.2 C°. With density of 0.758, MTBE has a high solubility in water [1]. MTBE can be used to increase the Octane Number of gasoline. At the beginning of 80's, by discovering the undesirable effects of tetra ethyl lead usage in fuel, MTBE started to be used worldwide. Nowadays MTBE forms about 15% of total fuel volume [2]. Gradually the undesirable effects of MTBE on environment had been revealed. MTBE leakage into soil, surface water or groundwater can pollute them and therefore make them unusable for farming activities or domestic demands.

There are many technologies for MTBE removal from polluted water [3, 4, 5, 6, 7 and 8]. Adsorption is the most conventional and economical technology [9] and would be discussed in this paper. Adsorption is a unit operation in which soluble components come out from solvent by an interphase mass transfer and transferred into surface of adsorbent [10]. Activated carbon adsorption has been widely considered as a potential treatment for removing organic matters from wastewater as it has a strong affinity for adsorption of organic substances even at low concentration [11, 12].

2. MATERIAL AND METHODS

In order to find the optimal conditions for adsorption of MTBE on any one of the adsorbents, some experiments have been carried out in an experimental setup as shown in figure 1. In each run, 1 liter of water polluted with MTBE with a certain initial concentration is poured in 5 capped glass containers and the pH value in each container is adjusted at the decided level by adding sulfuric acid or sodium hydroxide and the temperature is adjusted by a hot plate heater. A certain weight of the adsorbent is poured into every five containers and the solution is stirred by a magnetic stirrer (manufactured by Cenco Company under serial No. 34518). For obtaining the optimal pH, the experiments are carried out simultaneously and at the same temperature for all five containers. Samples are taken in certain time intervals from all five containers. The optimal pH value for adsorption of each one of the adsorbents used in this study can be obtained by determining the concentration of MTBE in the samples and plotting the value of C/C_0 with time. After obtaining the optimal pH value, the experiments continue to find the optimal temperature. A certain weight of the adsorbent is put in the capped glass container and then 1 liter of water polluted by MTBE with the predetermined initial concentration and the optimal pH obtained in the previous stage is added to it. When the temperature of the solution reaches the desirable level samples are taken from the solution in certain time intervals and the concentration of MTBE in the samples is determined. This experiment is carried out in 5 various temperatures. The optimal temperature for the adsorption of MTBE by any one of the adsorbents is obtained by analyzing the collected data. Each experiment is repeated at least three times and the average of the results are reported.

Fig1- Experimental setup used for batch experiments

3. RESULTS

3.1 Determination of Optimal pH Value

Charts 1, 2 and 3 show the variation of C/C_0 with time for the pH range of 5 to 9 for GAC, PAC and HRC, respectively.

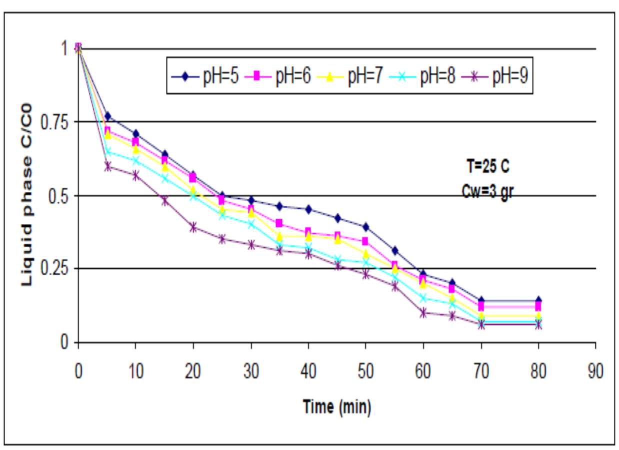


Chart1- Variation of C/C_0 ratio with time for GAC at various pH

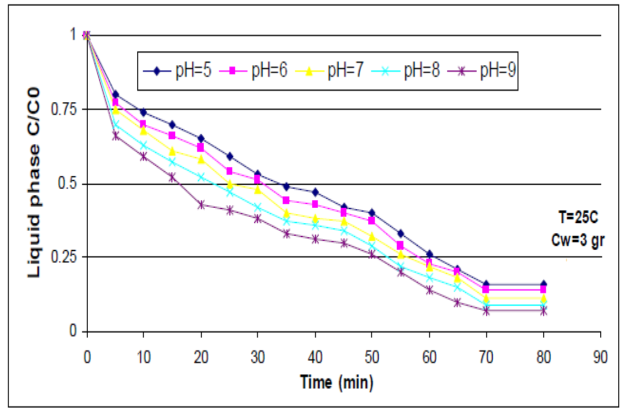


Chart2- Variation of C/C_0 ratio with time for PAC at various pH

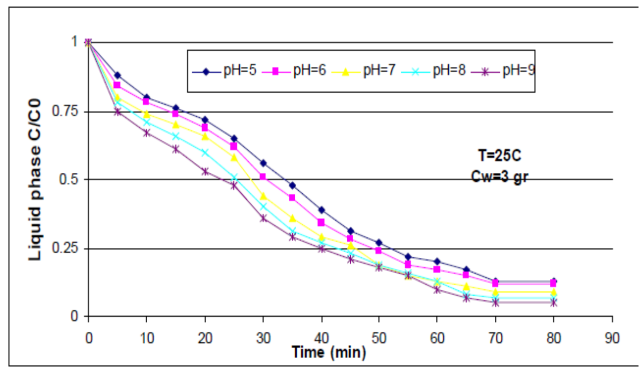


Chart3- Variation of C/C_0 ratio with time for HRC at various pH

3.2 Determination of the Optimal Temperature

Keeping the pH of the samples fixed at the value of 9, some experiments are carried out to determine the optimal temperature. Charts 4, 5 and 6 show the variation C/C0 with time for GAC, PAC and HRC for various temperatures, respectively.

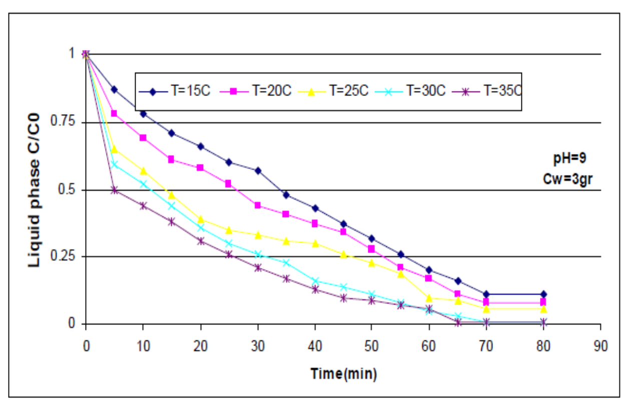


Chart4- Variation of C/C_0 with time for GAC at various temperatures

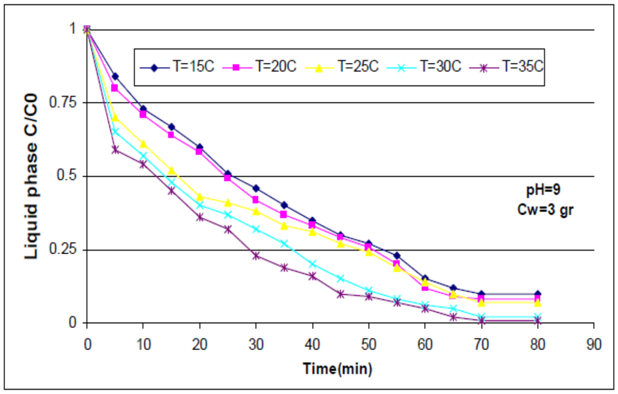


Chart5- Variation of C/C_0 with time for PAC at various temperatures

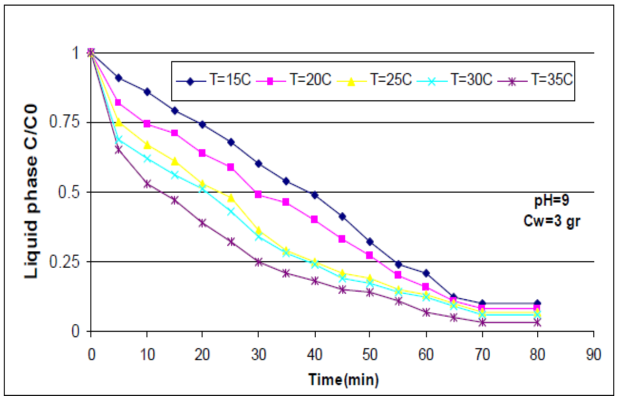


Chart6- Variation of C/C_0 with time for HRC at various temperatures

3.3 Comparison of the Performance of the Three Adsorbents

Chart 7 shows the variation of C/C_0 with time in the optimal operational conditions for various adsorbents.

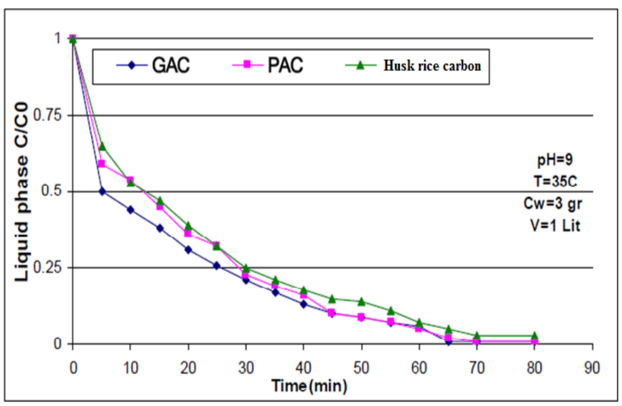


Chart 7- Variation of C/C_0 with time at the optimal operating conditions for various adsorbents

4. DETERMINATION OF ADSORPTION ISOTHERM EQUATIONS

After determination of optimal conditions of adsorption for the adsorbents used in batch experiments, the adsorption isotherm is obtained for these conditions. In order to determine the adsorption isotherm equations, the equilibrate concentration of MTBE on active carbon (q_{eq}) and equilibrate concentration of MTBE in liquid phase (C_{eq}) at various conditions are required. C_{eq} value is obtained by the data collected from the experiment as mentioned before. Then, the value of q_{eq} is calculated from relation 1 [13] knowing the parameters of optimal conditions for each adsorbent. Having the q_{eq} and C_{eq} values, and using the linear form of Freundlich and Longmuir adsorption isotherm equations as shown in relations 2 [14] and 3 [13], the constants of these adsorption isotherms could be obtained by plotting these linear equations for each adsorbent and determining the slope and ordinate of the plotted line in each case.

$$q_{eq} = \frac{V_0\left(C_0 - C_{eq}\right)}{C_w} \quad (1)[13]$$

$$q_{eq} = KC_{eq}^{n} \rightarrow \log\left(q_{eq}\right) = \log(K) + n\log\left(C_{eq}\right) \quad (2)[14]$$

$$q_{eq} = \frac{Kq^{\circ}C_{eq}}{1 + KC_{eq}} \rightarrow \frac{1}{q_{eq}} = \frac{1}{Kq^{\circ}C_{eq}} + \frac{1}{q^{\circ}} \quad (3)[13]$$

It can be observed that by conversion of Freundlich isotherm equation into a linear form and plotting the $\log(q_{eq})$ versus $\log(C_{eq})$, the slope of the line gives the *n* value, and the ordinate of the line gives log(K).

Moreover, by conversion of Longmuir isotherm equation into a linear form and plotting the $1/q_{eq}$ versus $1/C_{eq}$, the slope of the line gives $1/Kq^{\circ}$ and the ordinate gives $1/q^{\circ}$. To achieve adsorption isotherm equations in this study, batch experiments are carried out for six solutions with various initial concentrations at optimal operational conditions. In all batch experiments, the weight of adsorbent in testing containers was 3 g, and the volume of the solution was 1 liter.

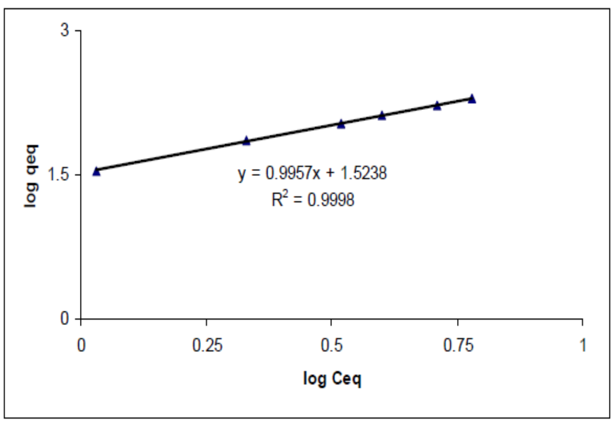
4.1 Granular Active Carbon (GAC)

The parameters required for determination of adsorption isotherm equations namely q_{eq} and C_{eq} were determined by carrying out batch experiments on six solutions with different MTBE initial concentrations in optimal operational conditions, and by using the adsorbent of GAC. These parameters are shown in Table 1.

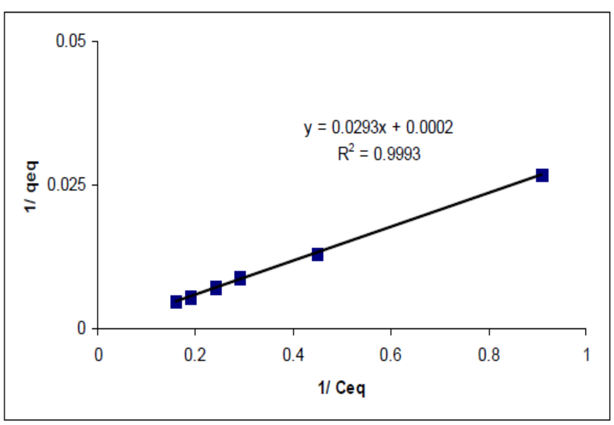
Table1- Equilibrium data for MTBE adsorption at optimal operational conditions for GAC

Number of Experiments	Solution Volume (Lit)	MTBE Initial Concentration (mg/L)	C_{eq} (mg/L)	q_{eq} (mg/L)
1	1	109/4	1/09	36/1
2	1	218/6	2/18	72/14
3	1	337/01	3/37	111/21
4	1	405/7	4/05	133/88
5	1	523/1	5/23	172/62
6	1	606/4	6/06	200/12

Using the data of Table 1 and equations 2 and 3, the linear forms related to Freundlich and Longmuir isotherms are plotted as illustrated in Chart 8



(a)



(b)

Chart 8- the linear forms related to (a) Freundlich and (b) Longmuir isotherm for GAC at optimal operating conditions

Using Chart 8, the constants of Freundlich and Longmuir adsorption isotherms coefficients can be obtained for the adsorption of MTBE on GAC. These values are presented in Table 2.

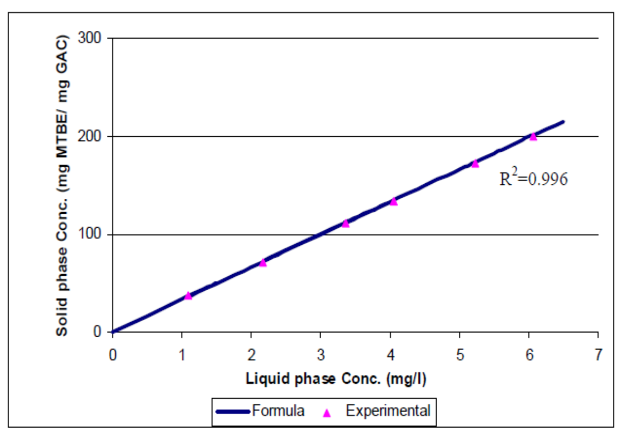
Table 2- The constants of Freundlich and Longmuir adsorption isotherms coefficients for GAC

Isotherm	Isotherm equation	Parameters
Freundlich	$q_{eq} = KC_{eq}^{n}$	K= 33.4041 n=0.9957
Longmuir	$q_{eq} = \dfrac{K\mathring{q}C_{eq}}{1+KC_{eq}}$	K= 0.00682 n=5000

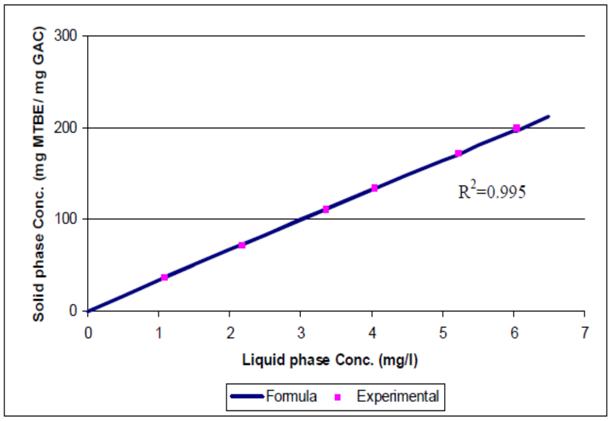
In order to assess the accuracy of Freundlich and Longmuir adsorption isotherm equations for the GAC, the adsorption isotherm equation plotted by using some other obtained experimental data are compared with the adsorption isotherm equation plotted by the constants obtained from Table 2. These validity diagrams are shown in Chart 9.

4-2- Powder Active Carbon (PAC)

The parameters required for determination of adsorption isotherm equations namely q_{eq} and C_{eq} were determined by carrying out batch experiments on six solutions with different MTBE initial concentrations in optimal operational conditions, and by using the adsorbent of PAC. These parameters are shown in Table 3.



(a)



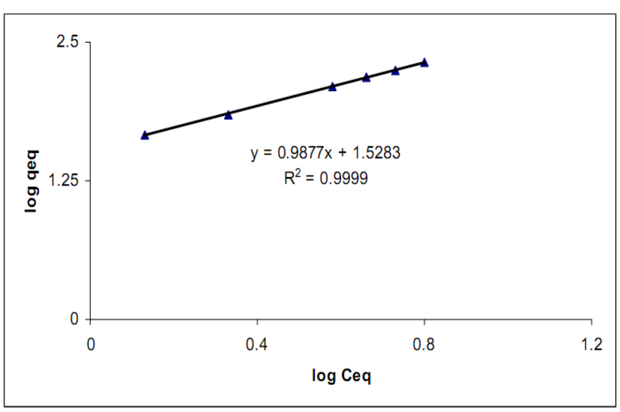
(b)

Chart 9- Checking validity of (a) Freundlich and (b) Longmuir isotherm for PAC

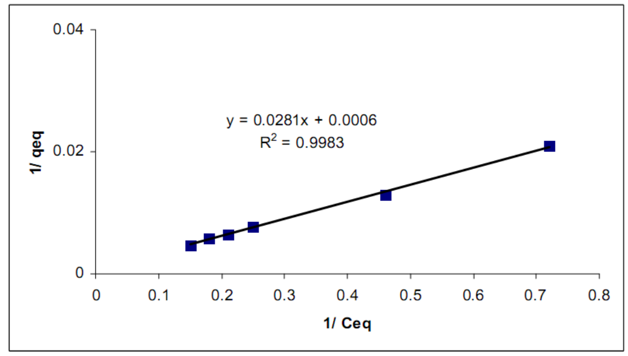
Table3- Equilibrium data for MTBE adsorption at optimal operational conditions for PAC

Number of Experiments	Solution Volume (Lit)	MTBE Initial Concentration (mg/L)	C_{eq} (mg/L)	q_{eq} (mg/L)
1	1	138/4	1/38	45/71
2	1	217/6	2/17	71/81
3	1	388/6	3/88	128/24
4	1	465/2	4/65	153/51
5	1	542/8	5/42	179/19
6	1	641/9	6/41	211/83

Using the data of Table 3 and equations 2 and 3, the linear forms related to Freundlich and Longmuir isotherms are plotted as illustrated in Chart 10.



(a)



(b)

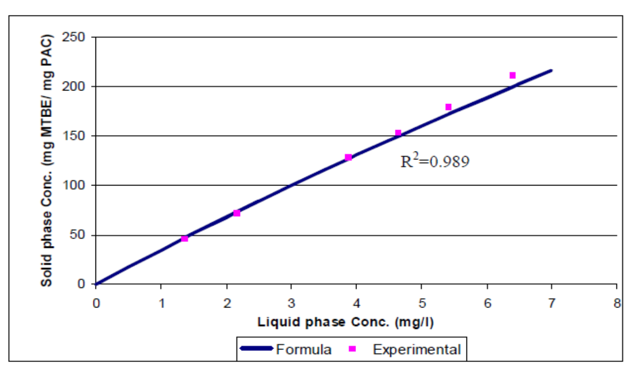
Chart 10- the linear forms related to (a) Freundlich and (b) Longmuir isotherm for PAC at optimal operating conditions

Using Chart 10, the constants of Freundlich and Longmuir adsorption isotherms coefficients can be obtained for the adsorption of MTBE on PAC. These values are presented in table 4.

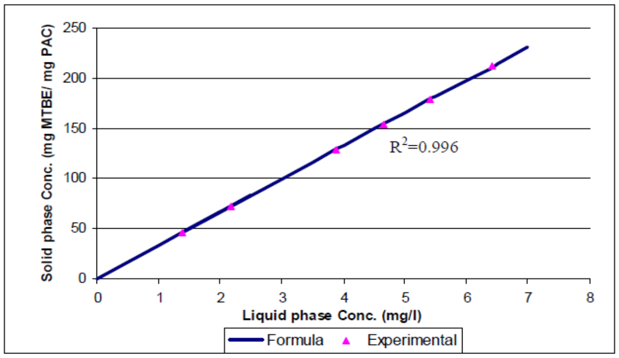
Table 4- The constants of Freundlich and Longmuir adsorption isotherms coefficients for PAC

Isotherm	Isotherm equation	Parameters
Freundlich	$q_{eq} = KC_{eq}^{n}$	K= 33.7520 n=0.9877
Longmuir	$q_{eq} = \frac{K\mathring{q}C_{eq}}{1+KC_{eq}}$	K= 0.0213 n=1666.666

Assessment of the accuracy of Freundlich and Longmuir adsorption isotherm equations for the PAC is carried out by comparing the adsorption isotherm equation plotted by using some other obtained experimental data with the adsorption isotherm equation plotted by the constants obtained from Table4. These validity Diagrams are shown in Charts 11.



(a)



(b)

Chart 11- Checking validity of (a) Freundlich and (b) Longmuir isotherm for PAC

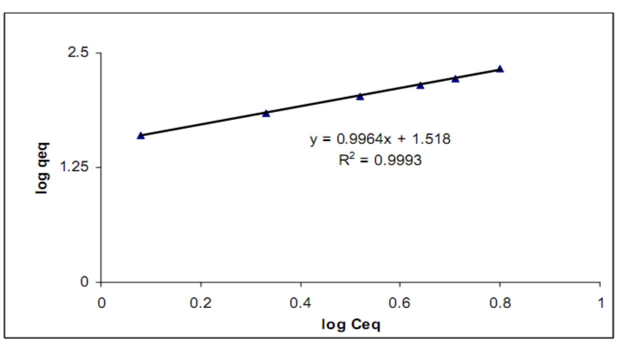
4.3 Husk Rice Carbon (HRC)

The parameters required for the determination of adsorption isotherm equations namely q_{eq} and C_{eq} were determined by carrying out batch experiments on six solutions with different MTBE initial concentrations in optimal operational conditions, and by using the adsorbent of HRC. These parameters are shown in Table 5.

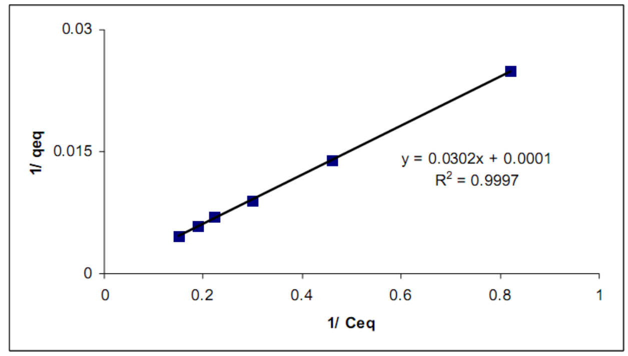
Table5- Equilibrium data for MTBE adsorption at optimal operational conditions for HRC

Number of Experiments	Solution Volume (Lit)	MTBE Initial Concentration (mg/L)	C_{eq} (mg/L)	q_{eq} (mg/L)
1	1	121/41	1/21	40/06
2	1	216/17	2/16	71/33
3	1	333/86	3/33	110/17
4	1	437/59	4/37	144/4
5	1	519/76	5/19	171/52
6	1	644/9	6/44	212/57

Using the data of Table 5 and equations 2 and 3, the linear forms related to Freundlich and Longmuir isotherms are plotted as illustrated in Chart 12.



(a)



(b)

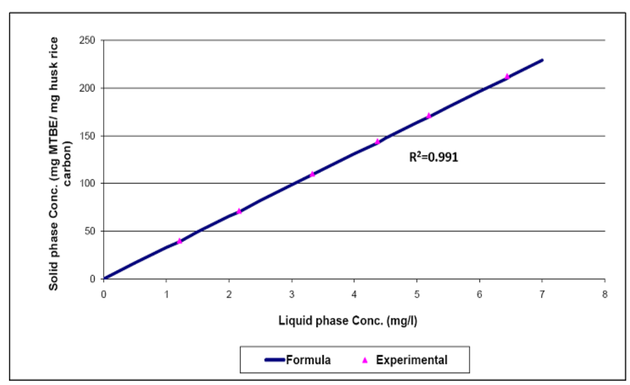
Chart 12- the linear forms related to (a) Freundlich and (b) Longmuir isotherm for HRC at optimal operating conditions

Using Chart 12, the constants of Freundlich and Longmuir adsorption isotherms coefficients can be obtained for the adsorption of MTBE on HRC. These values are presented in table 6.

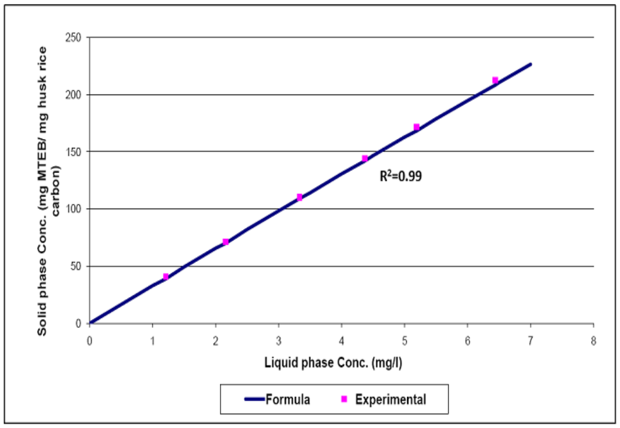
Table 6- fixed values of Freundlich and Longmuir adsorption isotherms coefficients for HRC in batch experiments

Isotherm	Isotherm equation	Parameters
Freundlich	$q_{eq} = KC_{eq}^{n}$	K= 32.9609 n=0.9964
Longmuir	$q_{eq} = \dfrac{K\mathring{q}C_{eq}}{1+KC_{eq}}$	K= 0.00331 n=1000

In order to assess the accuracy of Freundlich and Longmuir adsorption isotherm equations for the HRC, adsorption isotherm equation plotted by using some other obtained experimental data are compared with the adsorption isotherm equation plotted by the constants obtained from Table 6. These validity diagrams are shown in Chart 13.



(a)



(b)

Chart 13- Checking validity of (a) Freundlich and (b) Longmuir isotherm for HRC

CONCLUSIONS

Based on the data obtained for adsorption of MTBE on different adsorbents, the following points could be mentioned:
A- The effect of the kind of adsorbent: All three adsorbents used in this research showed great potentials for the adsorption of MTBE. GAC shows a better performance in MTBE adsorption compared to other adsorbents used in these experiments. Application of natural and available adsorbent of HRC is also well-justified on economic terms, as it is really cheap, and it can be used at industrial scales.

B- The effect of pH: The increase in the pH of the solution, results in the increase in MTBE adsorption. The reason can be justified by considering the equation of MTBE ionization in water as shown in relation 4, so that as the acidity decreases the OH^- ions concentration in the environment increases.

$$MTBE + H_2O \longleftrightarrow MTBE^+ + OH^- \quad (4)[10]$$

Considering relation 4, the increase in OH^- ions concentration causes the balance equation of MTBE ionization in water to be inclined toward converting the $MTBE^+$ ions to neutral MTBE molecules. This would result in the increase of neutral MTBE molecules concentration in the solution compared to the time when the acidity of the solution is higher. As the concentration of MTBE molecules in the solution increases, the adsorption rate of this substance also increases and, as a result, the MTBE concentration in the solution is decreased.

C. The effect of temperature: The increase in the temperature results in the increase of MTBE adsorption rate. This can be justified considering the direct relation between the temperature and the molecular diffusion coefficient. The increase in the temperature would result in the increase in molecular diffusion coefficient, and this in turn results in the increase of the molecular diffusion rate of the soluble material into active carbon and, as a result, the increase in adsorption rate.

D. Considering the accuracy assessment of Freundlich and Longmuir adsorption isotherm Diagrams for the three adsorbents, it can be observed that the error rate between the lab data and the data obtained from adsorption isotherm Diagrams is trivial and there is a quite sufficient conformity between them.

ACKNOWLEDGEMENTS

This research is supported by Shiraz Oil Refinery Company, Iran.

REFERENCES

[1]. European Union Risk Assessment Report – TERT-BUTYL METHYL ETHER, case No: 1634-04-4, 3rd Priority List, Volume: 19, 2002.
[2]. ITRC (The Interstate Technology & Regulatory Council) – Overview of Groundwater Remediation Technologies for MTBE and TBA- MTBE and Other Fuel Oxygenates Team, 2005. – [On line], <www.itrcweb.org >, [may 2009].
[3]. J. Sutherland, C. Adams, J. Kekobad- Treatment of MTBE by air stripping, carbon adsorption, and advanced oxidation: technical and economic comparison for five groundwaters, Water Research, 38 (2004) 193-205.
[4]. H. Lien, W. Zhang- Removal of methyl tert-butyl ether (MTBE) with Nafion, Journal of Hazardous Materials, 144 (2007) 194-199.
[5]. D. Pimentel-González, S. Revah, R. Campos-Montiel, O. Monroy-Hermosillo, E.J. Vernon-Carter- A laboratory study of the biodegradation of MTBE solubilized in water by a microbial consortium entrapped in a water-in-oil-in-water double emulsion, Process Biochemistry, 43 (2008) 1239-1243.
[6]. T. C. Shih, M. Wangpaichitr and M. Suffet- Evaluation of granular activated carbon technology for the removal of methyl tertiary butyl ether (MTBE) from drinking water- Water Research, 37 (2003) 375-385.
[7]. I.S. Jamall, T. X. Lu and J. C. Powers- Ex situ treatment of MTBE-containing groundwater by a UV peroxide system- Remediation Journal, 16 (2006) 71–80.
[8]. M. G. Ahunbay, O. Karvan and A.E.Şenatalar, MTBE adsorption and diffusion in silicalite-1- Microporous and Mesoporous Materials, 115 (2008) 93-97.
[9]. A.A. Keller, O.C. Sandall, R.G. Rinker, M.M. Mitani, B. Bierwagen, M. J. Snodgrass – Cost and Performance Evaluation of Treatment Technologies for MTBE-Contaminated Water, 2007. [On line] <www.tsrtp.ucdavis.edu/mtberpt/ vol.3.pdf> [Aug 2007].
[10]. O.Mowla, Feasibility Study of MTBE Physical Adsorption from Polluted Water on GAC, PAC and HRC, MSc thesis in Civil and Environmental Eng. department, Shiraz University, Supervised by: Dr. A. Karimi-Jashni, 2010.

[11]. A.H. Roy, “Activated carbon system for separation of liquids”, Hand book of separation technique for chemical engineering, 1997, pp. 1.587-1.618.
[12]. W. Xing, H.H. Ngo, S.H. Kim, S.Guo, P. Hagare, Adsorption and bioadsorption of granular carbon (GAC) for dissolved organic carbon (DOC) removal in wastewater, Bioresource Technology, 99 (2008) 8674-8678.
[13]. G. Tchobanoglous, F. Burton, H. Stensel, - Wastewater Engineering: Treatment and reuse- Metcalf & Eddy, Inc. 4th ed. – McGraw-Hill series in civil and environmental engineering, 2003.
[14]. F. Kano, I. Abe, H. Kamaya, I. Ueda, Fractal model for adsorption on activated carbon surfaces Langmuir and Freundlich adsorption, Surface Science, 467 (2000) 131-138.